

## Chromium(III) Complexes of a Tetraazamacrocyclic Ligand: Synthesis, Characterization and Antibacterial Investigation

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### Abstract

Biologically important macrocyclic compounds are getting a mentionable position in the research world due to their exhaustive applications in different sectors. On the other hand, chromium(III) is playing an analytical role by maturing the transition metal photochemistry and a biological role as an essential element for usual human body metabolism. Considering these facts, we carried out some studies on a number of chromium(III) complexes of an isomeric macrocyclic ligand and reported herein. Thus, two isomeric ligands, tet-a and tet-b were produced by the reduction of hexamethyl tetraazacyclotetradecadiene diperchlorate, Me<sub>6</sub>[14] diene.2HClO<sub>4</sub>. Reaction of tet-b with chromium(III) chloride yielded *cis*-[Cr(tet-b)Cl<sub>2</sub>]Cl which on substitution reaction afforded *cis*-[Cr(tet-b)(NCS)<sub>2</sub>](SCN), *cis*-[Cr(tet-b)(acac)](ClO<sub>4</sub>)<sub>2</sub>, *cis*-[Cr(tet-b)(ox)](ClO<sub>4</sub>) and *cis*-[Cr(tet-b)Br<sub>2</sub>]Br respectively. Axial substitution reactions on *cis*-[Cr(tet-b)Cl<sub>2</sub>]Cl with KI, NaNO<sub>2</sub> and KNO<sub>3</sub> in methanol furnished six coordinated greenish blue *cis*-[Cr(tet-b)I<sub>2</sub>]I and reddish violet *trans*-[Cr(tet-b)(NO<sub>2</sub>)<sub>2</sub>](NO<sub>2</sub>) and *trans*-[Cr(tet-b)(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>) respectively. The complex, *cis*-[Cr(tet-b)Cl<sub>2</sub>]Cl on reaction with NaOH followed by the addition of HClO<sub>4</sub> and NaClO<sub>4</sub> in aqueous solution produced *trans*-[Cr(tet-b)(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>). In all cases, the complexes were of six coordinated octahedral geometry. Different analytical and spectroscopic techniques were used for the characterization of the complexes. Antibacterial activities of the concerned ligand and complexes have been studied against four selected bacteria.

**Keywords:** Tetraazamacrocyclic Ligand; Chromium(III) Complexes; Spectral Studies; Antibacterial Activities

### Introduction

Development of azamacrocyclic complexes are undoubtedly one of the greatest invention in the research field of coordination chemistry [1,2]. Research interest in these compounds has grown during the past decades due to their wide range of applications in the advancement of pharmaceutical sciences [3,4]. In advance medical practice, macrocyclic complexes can be used as therapeutic agents [5], MRI contrast agents [6] and artificial restriction enzymes for cleaving DNA and RNA [7,8]. The complexes also act as

biochemical tools, such as they function as antibacterial [9], anti-fungal [10], anticancer [11] antitumor [12] and anti-proliferative [13] drugs in fighting against different infectious diseases. Studies on macrocyclic complexes also prove their unique properties, most importantly spectral, structural, electrochemical, kinetic and thermodynamic aspects [14,15].

Studies on copper(II), nickel(II), zinc(II), cadmium(II) and palladium(II) complexes of the concerned ligand, tet-b are available in literature [16-21]. Moreover, the preparation and charac-

terization of several  $cis$ -[Cr([14]-decane)(La)<sub>m</sub>](ClO<sub>4</sub>)<sub>n</sub> complexes containing auxiliary ligands, La (La= benzoate, chlorobenzoate, citrate, acetylacetonate, malonate or oxalate anion) [22,23] have been carried out. Ferromagnetic dihydroxo-bridged Cr(III)-Cu(II) and Cr(III)-Cu(II)-Cr(III) complexes, [Cr(tet-b)(OH)<sub>2</sub>Cu(bpy)(CH<sub>3</sub>OH)](ClO<sub>4</sub>)<sub>3</sub> and {Cu[Cr(tet-b)(OH)<sub>2</sub>]}(ClO<sub>4</sub>)<sub>4</sub> have also been reported in an earlier study [24]. Axial  $cis$ -substitution reaction on  $cis$ -[Cr(tet-b)Cl<sub>2</sub>]Cl to produce  $cis$ -[Cr(tet-b)(NCS)<sub>2</sub>](SCN),  $cis$ -[Cr(tet-b)(acac)](ClO<sub>4</sub>)<sub>2</sub>,  $cis$ -[Cr(tet-b)(ox)]ClO<sub>4</sub> and  $cis$ -[Cr(tet-b)Br<sub>2</sub>]Br was carried out as per literature [25] but the antibacterial activities of them were not investigated before. So in continuation of these studies, we prepared some new  $cis$  and  $trans$ -substituted chromium(III) complexes of the concerned macrocyclic ligand, tet-b and studied the antibacterial activities of all the mentioned Cr(III) complexes. Thus the present work concerns the synthesis and characterization of six-coordinated anion-bound Cr(III) complexes,  $cis$ -[Cr-(tet-b)I<sub>2</sub>]I and  $trans$ -[Cr(tet-b)(Y)<sub>2</sub>](Y) (Y=NO<sub>2</sub>, NO<sub>3</sub> or ClO<sub>4</sub>) and antibacterial activities of all the prepared Cr(III) complexes.

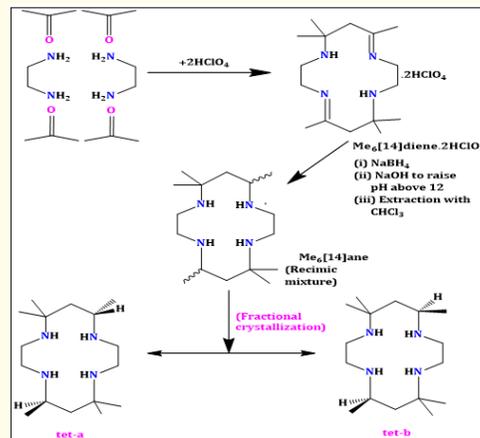
## Experimental Study

### Materials and equipment

Analytical reagent grade (Sigma Aldrich, USA) chemicals were used for the preparation of the complexes. Microanalysis of C, H and N have been carried out on a Leco CHNS-932 elemental analyzer (LECO Corporation, St. Joseph, MI) at the Department of Chemistry, Friedrich Schiller University, Jena, Germany. SYSTONIC electrothermal melting point apparatus was used to find melting points of the compounds. The infrared spectra of the metal complexes were taken as KBr disc in the range 4000-400 cm<sup>-1</sup> on a Shimadzu IR 20 spectrophotometer at the Department of Chemistry, University of Chittagong, Chattogram, Bangladesh. Conductance measurements of the metal complexes were done using HANNA instrument with HI 8820N conductivity cell. Electronic spectra of the samples were recorded on a Shimadzu UV-visible spectrophotometer. Magnetic measurements have been carried out by SHERWOOD SCIENTIFIC magnetic susceptibility balance.

### Ligand

Synthesis of the ligand salt, hexamethyl-tetraazacyclotetradecadiene dihydroperchlorate, Me<sub>6</sub>[14]diene.2HClO<sub>4</sub> (L.2HClO<sub>4</sub>) and its reduced isomeric ligands, tet-a and tet-b (Scheme 1) were carried out as procedure adopted in the literature [26].



Scheme 1

### Chromium(III) complexes of tet-b

#### Syntheses of the $cis$ complex, $cis$ -[Cr(tet-b)Cl<sub>2</sub>]Cl (S<sub>1</sub>) and its axial substitution products

The complex  $cis$ -[Cr(tet-b)Cl<sub>2</sub>]Cl (S<sub>1</sub>) and its axial  $cis$ -substitution products  $cis$ -[Cr(tet-b)(NCS)<sub>2</sub>](SCN) (S<sub>2</sub>),  $cis$ -[Cr(tet-b)(acac)](ClO<sub>4</sub>)<sub>2</sub> (S<sub>3</sub>),  $cis$ -[Cr(tet-b)(ox)](ClO<sub>4</sub>) (S<sub>4</sub>) and  $cis$ -[Cr(tet-b)Br<sub>2</sub>]Br (S<sub>5</sub>) were prepared as per literature [25].

#### Syntheses of $cis$ -[Cr(tet-b)I<sub>2</sub>]I (S<sub>6</sub>) and $trans$ -[Cr(tet-b)(Y)<sub>2</sub>](Y) (Y=NO<sub>2</sub> or NO<sub>3</sub>) (S<sub>7</sub> or S<sub>8</sub>)

The complex  $cis$ -[Cr(tet-b)Cl<sub>2</sub>]Cl (0.0570 g, 0.13mmol) was suspended in hot methanol (20 mL). Then KI (0.0431 g, 0.26 mmol), NaNO<sub>2</sub> (0.0179 g, 0.26 mmol) and KNO<sub>3</sub> (0.101g, 1mmol) was added separately to the hot suspension. After concentrating the mixtures on water bath, greenish blue  $cis$ -[Cr(tet-b)I<sub>2</sub>]I (S<sub>6</sub>), red-dish violet  $trans$ -[Cr(tet-b)(NO<sub>2</sub>)<sub>2</sub>](NO<sub>2</sub>) (S<sub>7</sub>) and  $trans$ -[Cr(tet-b)(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>) (S<sub>8</sub>) were formed respectively. The precipitates were filtered and washed with ethanol followed by diethylether and finally dried in vacuum.

For  $cis$ -[Cr(tet-b)I<sub>2</sub>]I (S<sub>6</sub>) (717.2): Color: Greenish blue. Anal. Calcd.(%) : C, 26.80; H, 5.06; N, 7.81. Found (%) C, 26.83; H, 5.03; N, 7.79. IR(KBr disc,cm<sup>-1</sup>): ν(N-H), 3165 s, ν(C-H), 2973 s, ν(CH<sub>3</sub>), 1383 s, ν(C-C), 1171 s, n(Cr- N), 430 s. Molar conductivity Ω(ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>): in DMSO, 77, in CH<sub>3</sub>CN 260. Magnetic moment μ<sub>eff</sub>(BM): 3.87. UV vis[λ<sub>max</sub> in nm (ε<sub>max</sub>)]: in DMSO, 584(106), 419(101), 385(90).

For *trans*-[Cr(tet-b)(NO<sub>2</sub>)<sub>2</sub>]NO<sub>2</sub> (S<sub>7</sub>) (474.5): Color: Reddish violet. Anal. Calcd.(%): C, 40.50; H, 7.65; N, 20.66. Found (%) C, 40.47; H, 7.60; N, 20.61. IR(KBr disc,cm-1):  $\nu$ (N-H), 3195 w,  $\nu$ (C-H), 2972 s,  $\nu$ (CH<sub>3</sub>), 1383 s,  $\nu$ (C-C), 1171 s,  $\nu$ (Cr-N), 440 s,  $\nu_{\text{asym}}$ (NO<sub>2</sub>), 1441 m,  $\nu_{\text{sym}}$ (NO<sub>2</sub>), 1315 m,  $\nu$ (N=O), 1485,  $\nu$ (NO), 1102. Molar conductivity  $\Omega$ (ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>): in DMSO, 77; in CHCl<sub>3</sub>, 0; in H<sub>2</sub>O, 290. Magnetic moment  $\mu_{\text{eff}}$ (BM): 3.87. UV vis [ $\lambda_{\text{max}}$  in nm ( $\epsilon_{\text{max}}$ ): in DMSO, 531(120), 457(77), 371(254); in CHCl<sub>3</sub>, 553(89), 371(236); in H<sub>2</sub>O, 542(66), 389(85).

For *trans*-[Cr(tet-b)(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>) (S<sub>8</sub>) (522.5): Color: Reddish violet. Anal. Calcd.(%): C, 36.78; H, 6.94; N, 18.76. Found (%) C, 36.81; H, 6.98; N, 18.75. IR(KBr disc,cm-1):  $\nu$ (N-H), 3240 vs,  $\nu$ (C-H), 2973 s,  $\nu$ (CH<sub>3</sub>), 1383 s,  $\nu$ (C-C), 1129 s,  $\nu$ (Cr-N), 451 s,  $\nu$ (NO<sub>3</sub>), 1456m, 1340 m. Molar conductivity  $\Omega$ (ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>): in DMSO, 98; in H<sub>2</sub>O, 232; in CH<sub>3</sub>CN, 262. Magnetic moment  $\mu_{\text{eff}}$ (BM): 3.85. UV vis [ $\lambda_{\text{max}}$  in nm ( $\epsilon_{\text{max}}$ ): in DMSO, 586(46), 411(29), 384(137); in H<sub>2</sub>O, 535(69), 386(55), 309(162).

### *trans*-[Cr(tet-b)(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>) (S<sub>9</sub>)

*cis*-[Cr(tet-b)Cl<sub>2</sub>]Cl (0.0265 g, 0.06 mmol) complex was suspended in 10 mL of water. Then 1 mL of 0.1 M NaOH was added to the solution while the solution turned blue. This blue solution was neutralized by adding small amount of HClO<sub>4</sub>. Then excess NaClO<sub>4</sub> (0.3 g) was added to the solution and after concentrating the solution reddish product, *trans*-[Cr(tet-b)(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>) (S<sub>9</sub>) was filtered off, washed with cold water, then with methanol followed by diethylether and finally dried in vacuum.

For *trans*-[Cr(tet-b)(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>) (S<sub>9</sub>) (634.8): Color: Red. Anal. Calcd.(%): C, 30.27; H, 5.72; N, 8.83. Found (%) C, 30.34; H, 5.77; N, 8.87. IR(KBr disc,cm-1):  $\nu$ (N-H), 3170 s,  $\nu$ (C-H), 2975 s,  $\nu$ (CH<sub>3</sub>), 1393 s,  $\nu$ (C-C), 1168 s,  $\nu$ (Cr-N), 447 s,  $\nu$ (ClO<sub>4</sub>), 1083m, 624 s. Molar conductivity  $\Omega$ (ohm<sup>-1</sup>cm<sup>2</sup>mole<sup>-1</sup>): in DMSO, 34; in H<sub>2</sub>O, 103. Magnetic moment  $\mu_{\text{eff}}$ (BM): 3.84. UV vis [ $\lambda_{\text{max}}$  in nm ( $\epsilon_{\text{max}}$ ): in DMSO, 551(153), 385(132); in H<sub>2</sub>O, 521(19), 383(138).

### Antibacterial studies

Study on antibacterial activity of isomeric macrocyclic ligand, tet-b and its chromium(III) complexes were performed by using disc diffusion method for controlling pathogenic microorganisms of animals and plants. Solutions of known concentration (1.0 mg/mL) of the test samples were made by dissolving measured amount

of the samples in definite volume of solvents. Dried and sterilized filter paper disc (4 mm in width) are then impregnated with known amounts of test substances by using micropipette and these were then allowed to dry. Discs containing the test material were placed on nutrient agar medium uniformly seeded with the test microorganism. Discs absorbed in respective solvent without test material are used as negative control. These plates were then kept at low temperature (4°C) for 2-4 hours to allow maximum diffusion. During this time dried discs absorb water from the surrounding media and then the test materials are dissolved and diffused out of the media. The diffusion happens as per the physical law that controls the diffusion of molecules through agar gel. Therefore, there is a continuous difference in test materials concentration in the media surrounding the discs. The plates were then incubated at 37°C for 48 hours to allow maximum growth of the organisms. If the test materials have any antibacterial action, it would inhibit the growth of the microorganisms giving a clear distinct zone called, "zone of inhibition". The antibacterial activities of the test agents were determined by measuring the zone of inhibition expressed in millimeter in diameter. The experiment was carried out thrice and mean of the reading was taken.

## Results and Discussion

### Ligand

The isomeric ligand 'tet-b', (Scheme 1) was prepared and characterized as per literature [26].

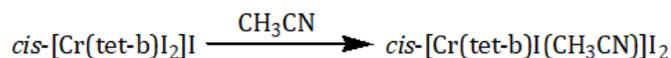
### Chromium(III) complexes

The complex *cis*-[Cr(tet-b)Cl<sub>2</sub>]Cl and some *cis*-substitution products of *cis*-[Cr(tet-b)Cl<sub>2</sub>]Cl: *cis*-[Cr(tet-b)(NCS)<sub>2</sub>](SCN), *cis*-[Cr(tet-b)(acac)](ClO<sub>4</sub>)<sub>2</sub>, *cis*-[Cr(tet-b)(ox)](ClO<sub>4</sub>) and *cis*-[Cr(tet-b)Br<sub>2</sub>]Br were prepared and characterized as per literature [25].

### *cis*-[Cr(tet-b)I<sub>2</sub>]I

Interaction of *cis*-[Cr(tet-b)Cl<sub>2</sub>]Cl with KI in methanol produced six coordinated octahedral greenish blue *cis*-[Cr(tet-b)I<sub>2</sub>]I complex. The Infrared spectrum of this complex displayed characteristic band at 3165 cm<sup>-1</sup>, 2973 cm<sup>-1</sup>, 1383 cm<sup>-1</sup>, 1171 cm<sup>-1</sup> and 430 cm<sup>-1</sup> for  $\nu$ (N-H),  $\nu$ (C-H),  $\nu$ (CH<sub>3</sub>),  $\nu$ (C-C) and  $\nu$ (Cr-N) respectively. Since the IR spectral band could not be run below 400 cm<sup>-1</sup>, so Cr-I stretch could not have been detected. The molar conductivity value 77 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup> in DMSO indicates that the complex is 1:1 elec-

trolyte as expected for the formula assigned. However the conductance value of  $260 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in acetonitrile corresponding to 1:2 electrolytes is probably due to the replacement of iodide ion by solvent molecule from the coordination sphere [27]. This replacement reaction can be expressed by the following expression:

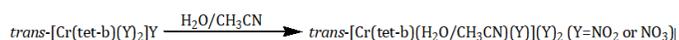


In electronic spectra of macrocyclic complexes of Cr(III) exhibit three absorption bands at 598-583, 390-380 and 345-340 nm due to  ${}^4\text{B}_{1g} \rightarrow {}^4\text{E}_{g(a)}$ ,  ${}^4\text{B}_{1g} \rightarrow {}^4\text{E}_{g(b)}$  and  ${}^4\text{B}_{1g} \rightarrow {}^4\text{A}_{2g}$  transitions respectively [28]. In DMSO the present complex, *cis*-[Cr(tet-b)I<sub>2</sub>]I displayed a sharp d-d band at 584 nm, a medium band at 419 nm and a very small band at around 385 nm. The positions of these bands are consistent with a distorted octahedral geometry with D<sub>4h</sub> symmetry [28]. The bands at 584 nm and 385 nm may be assigned to  ${}^4\text{B}_{1g} \rightarrow {}^4\text{E}_{g(a)}$  and  ${}^4\text{B}_{1g} \rightarrow {}^4\text{E}_{g(b)}$  transitions respectively. The magnetic moment value,  $\mu_{\text{eff}} = 3.87$  corresponds to d<sup>3</sup> system of chromium(III) ion [29]. Thus, the structure-I (Chart 1) can be assigned to *cis*-[Cr(tet-b)I<sub>2</sub>]I.

#### *trans*-[Cr(tet-b)(Y)<sub>2</sub>]Y (Y=NO<sub>2</sub> or NO<sub>3</sub>)

The complex *cis*-[Cr(tet-b)Cl<sub>2</sub>]Cl underwent axial substitution reactions with NaNO<sub>2</sub> and KNO<sub>3</sub> in methanolic solution to afford reddish violet *trans*-[Cr(tet-b)(NO<sub>2</sub>)<sub>2</sub>](NO<sub>2</sub>) and *trans*-[Cr(tet-b)(NO<sub>2</sub>)<sub>2</sub>](NO<sub>3</sub>) respectively. Infrared spectra of these complexes showed  $\nu(\text{N-H})$ ,  $\nu(\text{C-H})$ ,  $\nu(\text{CH}_3)$ ,  $\nu(\text{C-C})$  and  $\nu(\text{Cr-N})$  stretching bands at the expected regions. The complex *trans*-[Cr(tet-b)(NO<sub>2</sub>)<sub>2</sub>](NO<sub>2</sub>) displayed the  $\nu_{\text{asym}}(\text{NO}_2)$  band at  $1441 \text{ cm}^{-1}$ ,  $\nu_{\text{sym}}(\text{NO}_2)$  at  $1320 \text{ cm}^{-1}$ . Moreover the complex exhibited two bands; one at  $1485 \text{ cm}^{-1}$  due to  $\nu(\text{N=O})$  and the other at  $1102 \text{ cm}^{-1}$  assignable to  $\nu(\text{NO})$ , which are as expected for O-bonded nitrito complexes [30]. It may be noted that folding of a 14-membered macrocycle is possible only along a fold axis passing through diagonally opposite nitrogen atoms having their hydrogens lying on the same side [31]. The macrocycle can then fold away from the direction in which the NH hydrogens lie. Though some of the structures do have fold axes but due to steric constraints of two non-linear NO<sub>2</sub><sup>-</sup> groups, accommodation of two NO<sub>2</sub><sup>-</sup> groups in the *cis* position is not favorable [25,32]. Thus in this case a *trans* configuration is suggested for this complex. The other complex *trans*-[Cr(tet-b)(NO<sub>2</sub>)<sub>2</sub>](NO<sub>3</sub>), displayed bands at  $1456 \text{ cm}^{-1}$  and  $1340 \text{ cm}^{-1}$  attributed to coordinated NO<sub>3</sub><sup>-</sup> group. The separation of these bands by  $116 \text{ cm}^{-1}$  can be accounted for unidentate mode of coordination [33,34]. The spectrum further exhibited

a band around  $1383 \text{ cm}^{-1}$  (overlapped with CH<sub>3</sub> band) due to ionic NO<sub>3</sub><sup>-</sup> group which supports the presence of an ionic nitrate [34]. For both complexes the expected band at around 360- 250  $\text{cm}^{-1}$  due to  $\nu(\text{Cr-O})$  [35,36] could not have been detected as the spectra could not be measured below  $400 \text{ cm}^{-1}$ . For these complexes, molar conductivity values  $77\text{-}98 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  in DMSO (the color remained intact) indicated that these complexes are 1:1 electrolytes as expected for the formulae assigned. However the conductivity value  $0 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  for *trans*-[Cr(tet-b)(NO<sub>2</sub>)<sub>2</sub>](NO<sub>2</sub>) in chloroform corresponding to nonelectrolyte apparently indicates the incorporation of outer NO<sub>2</sub><sup>-</sup> in coordination sphere which should increase the coordination number of Cr(III) from 6 to 7, but practically it rather indicates the anion association in the coordination sphere [37]. On the other hand, the conductance values of  $232\text{-}290 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in water and  $262 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  in acetonitrile for *trans*-[Cr(tet-b)(NO<sub>2</sub>)<sub>2</sub>](NO<sub>3</sub>) corresponding to 1:2 electrolytes are probably due to the replacement of Y ion by solvent molecule while the water or acetonitrile molecules force the anion to come out from the coordination sphere [27]. This replacement reaction can be expressed by the following expression:



UV-Vis spectra of these complexes explored three absorption bands at 531-586 nm, 411-457 nm and 371-389 nm for respective transitions of octahedral geometry as expected [28]. The magnetic moment values of 3.85 and 3.87 of these complexes are an indication of paramagnetism corresponding to three unpaired electrons as expected for octahedral chromium(III) complexes with d<sup>2</sup>sp<sup>3</sup> hybridization [29]. Thus, the structure-II and structure-III (Chart 1) can be assigned to *trans*-[Cr(tet-b)(NO<sub>2</sub>)<sub>2</sub>](NO<sub>2</sub>) and *trans*-[Cr(tet-b)(NO<sub>2</sub>)<sub>2</sub>](NO<sub>3</sub>) respectively.

#### *trans*-[Cr(tet-b)(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)

The complex *cis*-[Cr(tet-b)Cl<sub>2</sub>]Cl interacted simultaneously with NaOH, HClO<sub>4</sub> and NaClO<sub>4</sub> in aqueous solution to yield *trans*-[Cr(tet-b)(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>). IR spectrum of this complex exhibited  $\nu(\text{N-H})$ ,  $\nu(\text{C-H})$ ,  $\nu(\text{CH}_3)$ ,  $\nu(\text{C-C})$  and  $\nu(\text{Cr-N})$  stretching bands at the expected regions. However the bands at  $1083 \text{ cm}^{-1}$  and  $624 \text{ cm}^{-1}$  indicated the presence of ClO<sub>4</sub><sup>-</sup> ion. The position as well as splitting of the band at  $1083 \text{ cm}^{-1}$  support the unidentate mode of coordination [38]. The molar conductivity value  $103 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$  in

water (in which color remained intact) of this complex indicated that this complex is 1:1 electrolyte [27] as expected for the formula assigned. However the conductivity value  $34 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1}$  determined for *trans*-[Cr(tet-b)(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>) in DMSO corresponding to nonelectrolyte may be due to anion (ClO<sub>4</sub><sup>-</sup>) association in the coordination sphere [37] as discussed in earlier section. From electronic spectral analysis three absorption bands were observed

at the expected regions which support octahedral geometry of the complex [28]. The magnetic moment value of this complex shows paramagnetism corresponding to three unpaired electrons as expected [29]. By considering all these analyses it can be assumed that accommodation of such two big ClO<sub>4</sub><sup>-</sup> ions in *cis* position is unfavorable [25,32]. Therefore, the structure-IV (Chart 1) can be assigned to *trans*-[Cr(tet-b)(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>).

**Chart 1:** Chromium(III) complexes of tet-b.

### Antibacterial activities

Antibacterial activities of the concerned isomeric macrocyclic ligand, tet-b and some of its complexes have already been studied [19-21]. It is noteworthy to examine whether the concerned ligand (tet-b) and its chromium(III) complexes against the concerned bacteria show any such activity or not. Reasonably, investigation on the antibacterial activities of the concerned metal salts, isomeric ligand, tet-b, its Cr(III) complexes and standard antibacterial agent have been carried out against two important gram-positive and two gram-negative bacteria which cause different fatal diseases. As per our earlier studies [20,21], the ligand, tet-b did not show any activity against the tested bacteria, but most of the complexes exhibited mentionable antibacterial activities. From this study, it is evident that most of the complexes were effective against both gram-positive and gram-negative bacteria (Table 1) but exception was found in case of diisothiocyanato (S<sub>2</sub>), acetylacetonato (S<sub>3</sub>) and

dinitrato (S<sub>8</sub>) complexes against *Pseudomonas aeruginosa* and dichlorido complex (S<sub>1</sub>) against *Klebsiella pneumonia* as they were fully inactive against the mentioned bacteria. On the other hand, dibromido (S<sub>5</sub>), dinitrito (S<sub>7</sub>) and diperchlorato (S<sub>6</sub>) complexes showed remarkable activity against almost all bacteria. The antibacterial activity of the metal salt and experimental solvent as control were also tested for the comparison. It was found that the experimental solvent has no effect on the growth of bacteria but metal salt showed the activity to a little extent against two gram positive and one gram negative bacteria. Though the metal salt exhibited some activity, but the activity explored by complexes is not due to metal ions. Because the complexes are very much stable. Thus there is no possibility of dissociation of complexes to release metal ions [39]. So based on the positive results of this investigation it can be concluded that further studies are warranted with the concerned macrocyclic ligands and their chromium(III) complexes.

Sample no.	Ligand and Chromium(III) complexes	Gram-positive bacteria		Gram-negative bacteria	
		<i>B. cereus</i>	<i>B. subtilis</i>	<i>K. pneumoniae</i>	<i>P. aeruginosa</i>
tet-b	tet-b	0	0	0	0
S <sub>1</sub>	<i>cis</i> -[Cr(tet-b)Cl <sub>2</sub> ]Cl	10	10	0	9
S <sub>2</sub>	<i>cis</i> -[Cr(tet-b)(NCS) <sub>2</sub> ](SCN)	11	10	11	0
S <sub>3</sub>	<i>cis</i> -[Cr(tet-b)(acac)](ClO <sub>4</sub> ) <sub>2</sub>	10	11	8	0
S <sub>4</sub>	<i>cis</i> -[Cr(tet-b)(ox)](ClO <sub>4</sub> )	12	10	7	9
S <sub>5</sub>	<i>cis</i> -[Cr(tet-b)Br <sub>2</sub> ]Br	13	9	11	13
S <sub>6</sub>	<i>cis</i> -[Cr(tet-b)I <sub>2</sub> ]I	11	9	10	8
S <sub>7</sub>	<i>trans</i> -[Cr(tet-b)(NO <sub>2</sub> ) <sub>2</sub> ](NO <sub>2</sub> )	12	11	9	11
S <sub>8</sub>	<i>trans</i> -[Cr(tet-b)(NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )	8	11	11	0
S <sub>9</sub>	<i>trans</i> -[Cr(tet-b)(ClO <sub>4</sub> ) <sub>2</sub> ](ClO <sub>4</sub> )	11	12	11	8
	CrCl <sub>3</sub> ·6H <sub>2</sub> O	5	6	0	6
	DMSO(Control)	0	0	0	0

**Table 1:** Antibacterial activities of ligand and its chromium(III) complexes.

## Conclusion

This study exposes that the concerned isomeric ligand, tet-b undergoes facile complexation with CrCl<sub>3</sub>·6H<sub>2</sub>O in DMF solvent to produce *cis*-[Cr(tet-b)Cl<sub>2</sub>]Cl which on substitution reactions furnished *cis*-[Cr(tet-b)(NCS)<sub>2</sub>](NCS), *cis*-[Cr(tet-b)(acac)](ClO<sub>4</sub>)<sub>2</sub>, *cis*-[Cr(tet-b)(ox)](ClO<sub>4</sub>), *cis*-[Cr(tet-b)Br<sub>2</sub>]Br, *cis*-[Cr(tet-b)I<sub>2</sub>]I, *trans*-[Cr(tet-b)(NO<sub>2</sub>)<sub>2</sub>](NO<sub>2</sub>), *trans*-[Cr(tet-b)(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>) and *trans*-[Cr(tet-b)(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>) complexes. It is interesting to note that *trans*-derivatives could be prepared from *cis*-complex. All the prepared complexes were tested against bacteria and most of the complexes exhibited good activity.

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## Conflict of Interest

There is no conflict of interest.

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